

Unsolved Problems of Structural Chemistry

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Linus Pauling, Theodore William Richards Medalist for 1947, has made notable contributions to quantum mechanics, valence theory, crystal structure, and also to electron diffraction

As I consider our present knowledge of structural chemistry, and compare it with that of 25 years ago, I am astonished at the progress that has been made, and almost tempted to feel that the major problems have been solved, and that the future developments of structural chemistry may be far less interesting than the developments which we have watched during the past quarter century. Twenty-five years ago we had no precise knowledge of interatomic distances and bond angles in molecules, and the understanding of the nature of the forces responsible for chemical combination was very vague. Now the detailed atomic structures of many hundreds of molecules and thousands of crystals are known, and the theory of valence and the chemical bond, with its basis in quantum mechanics, has developed far enough to permit reliable predictions to be made in many cases.

Despite this progress, there remain many unsolved problems. I shall discuss some of these problems, dividing them into four successive categories.

Comic-Strip Science

In our present atomic age everyone is continually made aware of the existence of atoms and molecules. Atomic fission and other atomic phenomena are presented to the younger generation in the comic papers, and molecules and their properties are introduced to us in advertisements. The schoolboy now accepts the existence of atoms and molecules without question, and he is apt to have a reasonably good understanding of their properties and significance before undertaking the study of science in school. I have noticed that the advertisements in our national magazines sometimes present problems, problems that have remained unsolved. One of the problems which has interested me is the nature of "pin-point carbonation." I have been given the impression that this phenomenon is interesting and valuable, but I have not been able to discover its nature. Another phenomenon of which I have tried, without success, to obtain an understanding is the "activation" of chlorophyll in the household deodorizer "Airwick." The selection of chlorophyll to be used in this preparation is no doubt to be attributed to its well-known ability to purify the air by converting carbon dioxide to oxygen. I have been interested in the properties of chlorophyll for some time, and I had not heard from other

sources about the activation of chlorophyll. By obtaining a copy of a patent I learned that chlorophyll is activated by formaldehyde. This type of activation seems to differ somewhat from ordinary types, because a great many molecules of formaldehyde are required for the activation of each molecule of chlorophyll. The thought has occurred to me that the significant phenomenon may really be one of deactivation, rather than activation, and that the formaldehyde may be acting in a way similar to that effective when it is used in embalming fluid.

Some Puzzling Small Problems

There are many molecules, even rather simple ones, whose structures have not yet been determined reliably, or about which there exists a difference of opinion. One of these is the ozone molecule. Spectroscopic data have been interpreted in recent years as showing that the ozone molecule consists of two oxygen atoms close together, and a third one farther away, and equidistant from the first two. This structure would be described as an oxygen molecule with a third oxygen atom only loosely bonded to it. The alternative structure of ozone (analogous to the structure of sulfur dioxide) is that in which a central oxygen atom is attached to two equidistant oxygen atoms, with a bond angle of about 125° , corresponding to the presence of a double bond and a single bond, in resonance. This structure, originally suggested by G. N. Lewis and substantiated by the electron-diffraction investigation carried out by W. Shand, Jr., and R. A. Spurr (1), is the correct one, but it is difficult to understand the contradictory conclusions reached by the spectroscopic investigators.

Another molecule about which there has been a difference of opinion is diborane, B_2H_6 . The alternative structures for this molecule are a structure similar to ethane, and a structure in which two hydrogen atoms are shared between the two boron atoms. The experimental evidence favors the second of these structures. In particular, an electron-diffraction investigation of tetramethyldiborane carried out by V. Schomaker and W. Shand, Jr., provides strong support for this structure. These investigators have found that the four methyl groups are essentially coplanar with the two boron atoms, with bond angles of approximately 120° and boron-carbon distance of 1.59 Å. The boron-

boron distance is about 1.85 Å. I think that this structure may be described in various ways, as, for example, by saying that there is a protonated double bond (E. Wiberg, K. S. Pitzer). My own inclination is to describe the molecule in terms of resonating bonds. If it is assumed that the bonds between the methyl carbon atoms and the boron atoms are single covalent bonds, then there are enough electrons for two additional electron-pair bonds to be formed, and there are five positions available for these bonds, one between two boron atoms, and four between boron and hydrogen atoms. If these bonds resonate equally among these positions, each position would be occupied by a bond with bond number 0.4. With the relation which I have recently suggested between interatomic distance and bond number, we then predict the distances $B-B = 1.85$ Å, exactly the value reported from the electron-diffraction investigation, and $B-H = 1.35$ Å.

A problem of a different sort in the field of inorganic chemistry is that of explaining the nonexistence of perbromic acid. It might be suggested that bromine lies just in the middle of the transition from a stable acid with coordination number 4, such as perchloric acid, $HClO_4$, to a stable acid with coordination number 6, such as paraperiodic acid, H_5IO_6 . However, the existence of salts of periodic acid with coordination number 4, such as KIO_4 , renders this explanation unsatisfactory.

Another interesting problem in inorganic chemistry is that of the structure of uninegative rhenium. The discovery by G. E. F. Lundell (2) that perrhenate ion in sulfuric acid solution is reduced by passage through a Jones reductor by eight stages, to rhenium with oxidation number -1, carries great interest because this is the only known occurrence of a metal with negative oxidation number, although compounds of metals with oxidation number 0, such as the nickel cyanide complex $Ni(CN)_4^{4-}$, have been made. The only explanation which I have been able to formulate for the existence of rhenium in this negative oxidation state is that the rhenium ion exists in this system with an electronic structure similar to that of bipositive platinum, which is isoelectronic with uninegative rhenium. Bipositive platinum exists only in complexes in which it forms four covalent bonds, with four groups arranged in a coplanar square about it. Accordingly, it seems likely that uninegative rhenium exists in the same state, and it may be that the four groups which it coordinates about itself at the corners of a square are four water mole-

cules. Experimental verification of this suggestion has not yet been obtained; the problem is now being attacked by E. Maun.

Some Larger Problems

There are a number of problems dealing with the structural chemistry of groups of substances which merit mention.

First, there is the question of the observed increase in coordination number of atoms which do not have a sufficiently large complement of electrons to permit the formation of electron-pair bonds in number permitted by the available bond orbitals. The boron hydrides, if we assume the new structures to be correct, are examples of this situation. Boron in BH_3 has only three valence electrons, permitting it to form three single covalent bonds. As a first-row element it has available for bond formation four bond orbitals. It might be expected that a polymer would be formed, diborane, in which all four bond orbitals are used, with the available electron pairs resonating among the bond positions; this description applies to the ethanellike structure for diborane. However, the alternative and presumably correct structure is one in which the bonds resonate among five bond positions about each boron atom. Similarly, in calcium hexaboride, in which there are enough electrons (assuming the presence of calcium ion) for $3\frac{1}{2}$ electron-pair bonds per boron atom, the configuration of the boron framework is such that each boron atom is bonded to five boron neighbors, instead of the four expected from the four available bond orbitals. Also, in boron carbide, B_4C , which is an electron-deficient structure with $3\frac{1}{2}$ electrons for every four atomic bond orbitals, each boron atom is surrounded by six atoms (either five boron atoms and a carbon atom or six boron atoms), and the carbon atoms are present as ketene groups $C=C=C$, with, however, the end carbon atoms having three boron neighbors apiece instead of the two that would be expected for the ketene bond structure (3). Similarly the molecules of platinum tetramethyl, $Pt_4(CH_3)_6$, in which there are electron pairs enough for quadrivalent platinum to form four single bonds, whereas the platinum atom has six stable d^2sp^3 bond orbitals, have been found by R. E. Rundle and J. H. Sturdivant (4) to have a resonating-bond structure in which each carbon atom has increased its coordination number to 5, with platinum having its normal coordination number of 6. The metals and intermetallic compounds, of course, provide an extremely large number of examples of structures of this sort, in which bonds resonate among a number of positions considerably greater than the number of bond orbitals available. A few years ago the general principle was expressed to me by V. Schomaker that when the number of electron pairs is less than the number of available bond orbitals reso-

nance of the electron pairs among several alternative positions occurs with an increase in the number of bond positions above the number of bond orbitals. This interesting general principle has not yet been given quantitative formulation (of the amount of increase in coordination number in relation to the amount of electron deficiency) or theoretical justification.

Another question in the field of inorganic chemistry about which little is known at present is that of the extent to which covalent bonds between metal atoms occur in nonmetallic compounds. I had thought that every chemist was familiar with one of the substances in which these bonds occur but a year or so ago I was astonished to learn, while telling a young man who had recently received his doctor's degree in chemistry about the enneacloroditungster complex ion, that he could not think of any common representative of this class of substances and, moreover, that he did not know what calomel is or what metals appear in the first group of the scheme of qualitative analysis.

The existence of the mercury-mercury bond in the mercurous ion, Hg_2^{++} , and in molecules such as $Cl-Hg-Hg-Cl$ has been recognized for many years, but until recently other examples of such bonds had not been reported. The complex ion $W_2Cl_9^{---}$ was discovered to have such a structure a few years ago by Cyril Brosset (5), when he determined the crystal structure of $K_3W_2Cl_9$ and isomorphous substances. This complex ion has a configuration obtained by sharing a face between two WCl_6 octahedra. The triangular face held in common by the two octahedra is large enough to permit the two tungsten atoms to approach one another to the small distance 2.46 Å, a distance smaller than that between tungsten atoms in metallic tungsten. Indeed, this distance interpreted by the equation connecting bond number and interatomic distance leads to the value 1.70 for the tungsten-tungsten bond number. The bond number for

each bond to the three chlorine atoms held in common is similarly calculated to be 0.5, and that of the bonds to the other chlorine atoms 0.7. The total number of bonds formed by the tungsten atom is thus calculated to be something over 5. The crystals are diamagnetic, and the bond structures which might be proposed for the complex of two tungsten atoms could accordingly be written $[:W-W: ; W=W, W=W:]$. The crystal structure of $K_3W_2Cl_9$ as reported by Brosset has recently been verified in our laboratories by Jürg Waser.

A closely similar structure has been found for iron nonacarbonyl by Powell and Ewens (6). The observed diamagnetism of this substance can be explained by the formation of a covalent bond between the two iron atoms, and the iron-iron distance, 2.46 Å, is only slightly larger than that expected for a single covalent bond.

The structure reported for crystals of molybdenum dioxide and tungsten dioxide by Arne Magnéli (7) also shows the presence of bonds between the metal atoms. These crystals have a distorted rutile structure, in which each metal atom is surrounded by an octahedron of oxygen atoms. The distortion from the ideal structure is of such a nature as to bring two molybdenum or tungsten atoms very close together to form a pair of atoms 2.48 Å apart, the corresponding edge shared by the two octahedra being greatly lengthened. The bond number calculated from this interatomic distance is 1.47, suggesting that there is an effort by each quadrivalent molybdenum or tungsten atom to use its two remaining valence electrons for the formation of a double bond with another atom of molybdenum or tungsten. The distance from the metal atom to the oxygen atom suggests resonance of about four covalent bonds among the six positions, causing the total valence of the molybdenum or tungsten atom to be approximately 6. In the corresponding crystals molybdenite, MoS_2 , and tungstenite, WS_2 , however, the metal atoms are so far apart that there is no bond formed between them.

There are many essentially nonmetallic crystals known in which metal atoms approach one another to within such distances as to correspond to significantly large fractional bond numbers, and there is little doubt that many of the physical and optical properties of the crystals are determined essentially by this closeness of approach. For example, the oxygen compounds containing iron seem to have a color which is correlated with the distance between iron atoms: pseudobrookite, Fe_2TiO_5 , and hematite, with iron-iron distance 2.88 Å, are red, whereas hydrated iron oxides such as lepidocrocite, goethite, limonite, and xanthosiderite tend to be lighter in color. The mineral cubanite, $CuFe_2S_4$, contains pairs of iron-sulfur tetrahedra in which the iron-iron distance, approximately 2.5 Å, corresponds to a bond number of 0.3. It was suggested by



the investigator of the crystal, M. J. Buerger (8), that this closeness of approach of iron atoms might be related to the unusual ferromagnetism shown by this sulfide mineral.

The theory of the color of dyes and other complex organic molecules has been rather well developed in recent years, and the color of these substances is reasonably well understood. However, little progress has been made in the development of a systematizing or correlating theory of the color of inorganic complexes. There is one set of substances which shows especially striking coloration. This is the set of substances containing the same element in two different valence states. Substances of this sort have been recognized for many years as having abnormally deep and intense coloration. For example, the complexes of cuprous copper with chloride ion, in solution in concentrated hydrochloric acid, are colorless, as is cuprous chloride itself, and the complexes of cupric copper with chloride ion are green. However, if cuprous and cupric solutions are mixed an intensely colored brown or black solution is obtained, apparently due to complexes containing both cuprous and cupric copper. Similarly, tervalent antimony chloride and quinquivalent antimony chloride are colorless, but a mixture of the two has a deep brown or black color. Crystals of $(\text{NH}_4)_2\text{SbCl}_6$, a black substance, have been investigated by x-rays by N. Elliott (9) and shown to have a structure indistinguishable from that of potassium chlorostannate. Moreover, the crystals are diamagnetic, so that the complexes cannot be SbCl_6^{--} , which would necessarily be paramagnetic because of the presence of an odd number of electrons, but must be alternately SbCl_6^{---} and SbCl_6^- . Crystals of cesium aurous auric chloride, $\text{Cs}_2\text{AuAuCl}_6$, which are also intensely black in color, have been studied with x-rays, and shown to contain the aurous complex AuCl_2^- , with linear configuration, and the square coplanar auric chloride complex AuCl_4^- (10). The existence of these two distinct complexes rules out the obvious suggestion that the intense color is due to the resonance of electrons among the atoms of the metal, in such a way as to give each atom a resonating structure in which it is a hybrid of two covalent states.

Another example of the phenomenon is observed often in the chemical laboratory when a solution containing ferrous ion is precipitated with alkali. Ferrous hydroxide is white, and ferric hydroxide is brown. When a ferrous solution is precipitated, however, the initially white precipitate is immediately partially oxidized by atmospheric oxygen, to form a ferrous ferric hydroxide, which is black in color (or deep green when finely divided).

A few years ago it was pointed out to me by Sterling Hendricks that ordinary black mica, biotite, which has an intensely black color, owes this color to the pres-

ence of iron in both the ferrous and ferric oxidation state. Black tourmalines also usually contain both ferrous and ferric iron. Another intensely black mineral, with black streak, is ilvaite, with composition $\text{Ca}(\text{Fe}^{++})_2\text{Fe}^{+++}(\text{SiO}_4)_2\text{OH}$.

Molybdenum blue and tungsten blue, which have intense deep blue coloration, have the formulas $\text{MoO}_{2.5-3}$ and $\text{WO}_{2.5-3}$. The tungsten bronzes also contain tungsten in an intermediate valence state; their formulas lie between the limits $\text{Na}_2\text{W}_2\text{O}_6$ and $\text{Na}_2\text{W}_3\text{O}_9$. Many metal oxides, such as Fe_3O_4 , U_3O_8 , and Pr_4O_{11} , may owe their black color to this phenomenon. However, it is interesting that the intermediate oxide Sb_2O_4 is white, although the halogen complexes of antimony with mixed valence are intensely colored.

The consideration of the color and other properties of ordinary complexes (not involving intermediate oxidation states) has recently led me to formulate a new rule, to the effect that half-full and full electronic shells in an atom are closely similar in properties. This rule applies not only to the ordinary shells such as the 3d subgroup of 5 orbitals in an isolated atom, but also to special subgroups of orbitals in atoms which form covalent bonds. For example, it applies to the set of three 3d orbitals available for unshared electrons in an atom of the first transition

period which forms six octahedral d^2sp^3 covalent bonds.

Examples of the similarity of half-full and full shells for isolated atoms or ions are not hard to find. The terpositive gadolinium ion, with seven 4f electrons, is colorless, and in this and other properties (except paramagnetism) it resembles the terpositive lutetium ion with fourteen 4f electrons. The bipoisitive europium ion and bipoisitive ytterbium ion, which similarly have a half-full and full 4f subshell, respectively, also have similar properties. A striking phenomenon is the abnormally large atomic volume shown by metallic europium and metallic ytterbium, and by no other rare-earth metal. This large atomic volume of these two metals is due to their acceptance of metallic valence 2, instead of the normal value of about 3 shown by the other rare-earth metals. The metallic valence 2 is correlated for europium with the achievement of a half-full 4f subshell and for ytterbium with the achievement of a full 4f subshell.

In transition elements forming six covalent bonds there are three 3d orbitals not used in bond formation. For example, in the complexes of terpositive cobalt these three 3d orbitals contain their full complement of six electrons, whereas in the complexes of terpositive chromium they contain three electrons. The extraordinarily close similarity in properties of the cobaltic complexes and chromic complexes is well known.

The same close similarity in properties is shown also by the corresponding complexes of heavier transition elements. Thus both potassium hexachlororhodate, K_3RhCl_6 , and potassium hexachloromolybdate, K_3MoCl_6 , form red crystals.

There are many striking examples of the existence of stable polynuclear inorganic complexes which deserve explanation. The existence of anions such as orthosilicate, $(\text{SiO}_4)^{---}$, disilicate, $(\text{Si}_2\text{O}_7)^{---}$, trisilicate $(\text{Si}_3\text{O}_{10})^{---}$, etc., ultimately leading by continued condensation to rings, infinite chains, and sheets of silicate tetrahedra, offers no significant problems at the present time. This process of condensation of simple acids to complex acids, with sharing of polyhedral elements, is well understood. Often, however, it is found that an element forms certain very complex polynuclear anions which show a striking stability, and clearly do not simply fit into a series of polymers of increasing complexity. One set of examples is the duodecimolybdic acids and the duodecitungstic acids, such as ordinary phosphomolybdic acid. Nearly 20 years ago I suggested a structure for these duodeci complexes in which a roughly spherical cage of twelve condensed octahedra was formed about a central phosphate ion or similar tetrahedral ion. It was then shown by Keggins that these duodeci complexes do possess a structure of this general sort, but with the twelve molybdenum or tungsten octahedra ar-

Ernest H. Volwiler

Ernest H. Volwiler, executive vice president of Abbott Laboratories, joins the list of six distinguished chemists who have preceded him as winners of the Honor Scroll Award of the American Institute of Chemists. Presentation took place Oct. 10 at a dinner of the Institute in Chicago honoring Dr. Volwiler for "his large number of contributions to the field of medicinal chemistry, for his outstanding work in the organization of research programs, and for his active work in furthering the work of scientific societies."

A member of the AMERICAN CHEMICAL SOCIETY since 1916, Dr. Volwiler has played an aggressive role in furthering the work of the Society. He is currently a director-at-large and has also served as chairman of the Division of Medicinal Chemistry, chairman of the Chicago Section, counselor, and counselor-at-large. During 1922-24, he edited the *Chemical Bulletin* of the Chicago Section.

Born in Hamilton, Ohio, in 1893, Dr. Volwiler was graduated from Miami University (Ohio) and received his Ph.D. from the University of Illinois in 1918. He joined Abbott Laboratories in 1920 as chief chemist after a brief teaching career and in 1946 he was made executive vice president, having been in charge of research since 1930.

ranged in a somewhat different way from that which I had proposed. I believe that many of the surprisingly complex stable anions formed by elements such as molybdenum, tungsten, vanadium, columbium, and tantalum have similar compact structures of condensed polyhedra.

An example of the complications which are introduced into inorganic chemistry by the stability of these unusual complexes can be seen by reading about the chemistry of molybdenum dichloride, MoCl_2 . When this substance is dissolved in water only one third of the chlorine is precipitable by silver ion. The electrolytic properties of the aqueous solution are also abnormal, and show the presence of an ion with large electrical charge. It was suggested long ago that the substance contains the complex $\text{Mo}_3\text{Cl}_4^{++}$. The difficulties of assigning a reasonable electronic structure to this complex caused me a few years ago to assume that the complex is $\text{Mo}_6\text{Cl}_8^{++++}$, and that molybdenum dichloride itself is to be assigned the formula $[\text{Mo}_6\text{Cl}_8]^{++++}\text{Cl}_4^{--}$. The ionic chlorine is easily replaced by other anions, such as bromide ion, hydroxide ion, and sulfate ion. In order to verify this suggestion Philip Vaughan in our laboratories has been making an x-ray investigation of two crystals thought to contain this complex, $(\text{NH}_4)_2[\text{Mo}_6\text{Cl}_8]\cdot\text{Cl}_6\cdot 2\text{H}_2\text{O}$ and $\text{H}_2[\text{Mo}_6\text{Cl}_8]\cdot\text{Cl}_6\cdot 6\text{H}_2\text{O}$. In the meantime, however, crystal structure determinations of two other substances, $[\text{Mo}_6\text{Cl}_8](\text{OH})_4\cdot 14\text{H}_2\text{O}$ and $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4\cdot 8\text{H}_2\text{O}$, have been reported by Cyrill Brosset (11). These crystals have been found to contain complexes with the expected structure. This structure is a very interesting one. The eight chlorine atoms are at the corners of a cube, and the six molybdenum atoms are a little displaced outward from the centers of the six faces of the cube. Presumably each molybdenum atom forms bonds with the four chlorine atoms which surround it in a square, nearly coplanar configuration, each chlorine atom thus being bonded to three molybdenum atoms. Inasmuch as bivalent molybdenum has two unshared electron pairs, the configuration suggests that the molybdenum atoms in this complex have an octahedral configuration with the unshared pairs at two opposite corners of the octahedron, one directed toward the center of the complex and one directed outward. This arrangement accordingly conforms to the general rule that an atom with some unshared pairs of electrons tends to form a coordination polyhedron, with some corners occupied by bonded atoms and others by unshared pairs.

I think that the compound $\text{Ta}_6\text{Br}_{14}$, studied by W. H. Chapin, may be somewhat similar in structure. This substance, in which tantalum has an average oxidation number of $2\frac{1}{3}$ (the color of the compound is deep green, corresponding to the intermediate oxidation state), contains the complex ion $\text{Ta}_6\text{Br}_{12}^{++}$, and the related emerald-green substance Ta_6Cl_4 contains

the complex ion $\text{Ta}_6\text{Cl}_{12}^{++}$. The two remaining halide ions are easily replaced by hydroxide ions or other anions. A reasonable structure for the complex is that in which the six tantalum atoms occupy the six corners of a regular octahedron, with the twelve halogen atoms near the centers of the twelve edges of the octahedron. With such a structure each tantalum atom is bonded to four halogen atoms, which lie at the corners of a square which may be nearly coplanar with the tantalum atom, and each halogen atom is bonded to two tantalum atoms. There are not two unshared electron pairs (four electrons) per tantalum atom to occupy the other two corners of an octahedral coordination polyhedron about tantalum, but only an average of $2\frac{1}{3}$ electrons. The significance of this electron number is not clear.

Vanadium, columbium, and tantalum form many compounds which can be represented as salts of oxygen acids containing six metal atoms. An example of a hexavanadate is sodium hexavanadate, $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$. A possible structure for the hexavanadate complex ion may be assigned by writing this formula $\text{Na}_2\text{V}_6\text{O}_{13}(\text{OH})_3$. If six vanadium atoms are placed at the corners of an octahedron and twelve oxygen atoms are placed out from the centers of the twelve edges of the octahedron, a thirteenth oxygen atom may then be located at the center of the octahedron, being thus bonded to all six vanadium atoms, and six hydroxyl groups may be placed directly out from the six vanadium atoms, completing the six octahedra. Hexacolumbates and hexatantalates also occur with similar formulas, such as $\text{K}_2\text{Cb}_6\text{O}_{16}(\text{OH})_3\cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{Ta}_6\text{O}_{13}(\text{OH})_3\cdot 2\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{Ta}_6\text{O}_{13}(\text{OH})_3\cdot 2\text{H}_2\text{O}$. Most of the salts of these acids, however, have formulas corresponding to the replacement of eight hydrogen atoms. Examples are $\text{K}_6\text{Cb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$, $\text{Na}_6\text{K}_2\text{Cb}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$, $\text{Na}_6\text{Ta}_6\text{O}_{19}\cdot 24\text{H}_2\text{O}$, $\text{K}_6\text{Ta}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$, $\text{Ag}_6\text{Ta}_6\text{O}_{19}\cdot 3\text{H}_2\text{O}$, and $\text{Mg}_6\text{Ta}_6\text{O}_{19}\cdot 9\text{H}_2\text{O}$. It seems likely that the hexacolumbate and hexatantalate ions in these crystals have the structure described above, with the hydrogen ions of the six hydroxyl groups replaced by metal.

Another structural problem of somewhat different sort is that presented by the complex ion Pb_9^{--} , which exists in liquid ammonia solutions containing sodium and lead, as was shown by C. A. Kraus. A possible structure for this complex is again a cubic structure, with eight lead atoms at the corners of the cube and one in the center of the cube. The lead atoms at the corners of the cube might be considered to be uninegative, analogous to bismuth, and with the power of forming three covalent bonds, extending along edges of the cube. A quadripesitive lead atom at the center of the cube would then cause the resultant charge on the complex to be correct. There would, of course, be bonds formed between the central lead atom and the surrounding atoms.

Some Great Problems

One great problem in structural chemistry which still awaits satisfactory solution is that of the structure of metals and intermetallic compounds. A small amount of progress has been made in correlating the composition of alloys such as the gamma alloys (Cu_5Zn_8 , $\text{Cu}_{31}\text{Sn}_8$, Al_3Cu_8 , $\text{Fe}_3\text{Zn}_{21}$, etc.) with the Hume-Rothery ratio of valence electrons to atoms, and with the electron numbers of Brillouin zones as calculated by quantum mechanical methods. Nevertheless, progress has not yet been great enough to permit confident predictions to be made about intermetallic compounds, nor to provide a satisfactory general theory of their composition, structure, and properties.

Another problem is that of the structure of activated complexes. The general quantum mechanical concept involving resonating bonds, as developed by Eyring and Polyani, is satisfying, but a general theory of the structure and stability of activated complexes still awaits formulation.

It may turn out that the problem of the structure of atomic nuclei may be considered a problem of structural chemistry. I do not know to what extent the available facts about the properties of nuclei indicate that the structure is a dynamic one, in which the nucleons cannot be assigned average positions relative to one another. It seems to me, however, that it is conceivable that the forces between nucleons involve attractive terms and repulsive terms in such a way as to cause the nucleons to assume average equilibrium positions relative to one another in the same way that atoms do in molecules and crystals, and that in the course of time the geometrical structures of atomic nuclei may be determined. A great contribution toward the solution could be made by obtaining diffraction data from atomic nuclei (starting with the deuteron, tritium nucleus, and alpha particle) by bombarding them with essentially monochromatic neutrons of high energy, approximately 30,000,000 electron volts.

In the field of organic and biological chemistry, it is my opinion that the structure of proteins and the origin of the specific properties of biological substances are the most important problems at the present time. The specificity of antigens and antibodies, of enzymes, and of genes will, I think, all be found to be due to the same modes of physical-chemical interaction between molecules. The evidence from the field of immunochemistry supports very strongly the concept that this biological specificity is due to a complementarity in structure of large molecules, and that the specific forces operate only when the complementary structures are in close contact with one another, with the surface atoms of the two structures approaching to within an Ångström or a few Ångströms before the forces become large. It is true

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The work is carried on with the advice and guidance of a committee called the Applied Mathematics Council, made up of representatives of government agencies and private organizations actively interested in the work of the unit.

The Institute of Numerical Analysis, on the campus of the University of California at Los Angeles, is being underwritten for the next two years by the Office of Naval Research. Its primary function is to conduct research and training in the types of mathematics which are pertinent to the efficient exploitation and development of high-speed automatic digital computing machinery.

The Computation Laboratory, also underwritten by the Office of Naval Research, includes the mathematical tables project of the Bureau of Standards. The unit is providing a general computing service of high quality and large capacity for private industry, government agencies, educational and research institutions.

The Statistical Engineering Laboratory provides a general consulting service on methods of modern statistical inference as applied to the engineering and physical sciences.

The Machine Development Laboratory is in charge of the development and construction of computing machines which will meet performance specifications established by the operating units of the Applied

Mathematics Laboratories, the Office of Naval Research, the Bureau of the Census, and other government agencies. At present it is setting up the mathematical specifications for two high-speed electronic computers being constructed through the Bureau of Standards for the Office of Naval Research and the Bureau of the Census at a cost of \$300,000 each. This organization is responsible for the coordination of mathematicians, electronics engineers, and physicists who must cooperate to produce this revolutionary equipment. When completed one of the machines will be installed at the Institute of Numerical analysis.

Directory of Ceramic Laboratories

A revision is being made of Bureau of Mines Information Circular 6999R, which lists commercial laboratories engaged in the analysis and testing of ceramic and mineral products. Directors of laboratories whose work falls in this category, and who have not recently received a questionnaire on this subject from the bureau, are asked to communicate with Morris Slavin, U. S. Bureau of Mines, College Park, Md., so that their laboratories may be included in the new list.

Mellon Institute

A brochure entitled "Postwar Research in Mellon Institute" is the thirty-fourth annual report of the director, E. R. Weidlein, to the board of trustees. Published in condensed form in C&EN, May 10, 1947, the full report is 38 pages in length. Copies can be obtained from Mellon Institute of Industrial Research, Pittsburgh 13, Pa.

Venture Capital

A brief description of the services and organization of a company incorporated in 1946 for the purpose of making venture capital more readily available for development of untried business enterprises of a scientific nature is contained in a pamphlet published by New Enterprises, Inc., 84 State St., Boston 9, Mass.

Structural Chemistry

(Continued from page 2978)

that this theory may seem to be incompatible with the work of A. Rothen (12), who has published experimental results interpreted as showing that under certain circumstances enzymes are able to exert their specific action through a film of polymer as much as 200 Å. thick. I do not have any explanation to offer for these experiments except the obvious one that the polymer film may not be completely intact and impenetrable, but I feel that the evidence for the theory that specific biological forces result from complementarity in structure and require very close approximation of the complementary structures for their operation is extremely strong, and I think it highly likely that this is the only mechanism of biological specificity which has been developed in living organisms.

The progress of science in recent years is bringing biology and medicine into closer and closer contact with the basic sciences, and I am confident that the next few decades will bring to us a detailed understanding of the molecular structure of biological systems, and that this understanding will help in the rapid general progress of biology and medicine.

References

- (1) J. Am. Chem. Soc., 65, 179 (1943).
- (2) *Rev. Standards J. Res.*, 18, 629 (1937).
- (3) G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.R.S.S.*, 32, 432 (1941) (in English);
- (4) K. Clark and J. L. Hoard, *J. Am. Chem. Soc.*, 65, 2115 (1943).
- (5) J. Am. Chem. Soc., 69, 1561 (1947).
- (6) Ark. Kon. Mineral. Geol., 12A, Nr. 4 (1935).
- (7) J. Chem. Soc., 1939, 286.
- (8) Ark. Kon. Mineral. Geol., 24A, Nr. 2 (1946).
- (9) J. Am. Chem. Soc., 67, 2056 (1945).
- (10) J. Chem. Phys., 2, 298 (1934); K. A. Jensen, *Z. anorg. allgem. Chem.*, 252, 317 (1944).
- (11) N. Elliott and L. Pauling, *J. Am. Chem. Soc.*, 60, 1846 (1938).
- (12) Ark. Kon. Mineral. Geol., 20A, Nr. 7 (1945); *Ibid.*, 22A, Nr. 11 (1946).
- (13) J. Biol. Chem., 163, 345 (1946); *Ibid.*, 167, 299 (1947); *Ibid.*, 168, 75 (1947).

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